

# PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

No. 6083, A.D. 1930.

## Manufacture of Intermediates and Dyes from Heterocyclic Nitrogen Compounds.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain and HENRY ALFRED PIGGOTT, and ERNEST HARRY RODD, both of Crumpsall Vale Chemical Works, Blackley, Manchester, both British Subjects, do hereby declare the nature of this invention to be as follows :—

This invention comprises the manufacture of new intermediate compounds and dyes of the polymethine series therefrom.

We have discovered that valuable new intermediate compounds and dyes are obtained by condensing heterocyclic nitrogen compounds containing reactive methyl groups or external reactive methylene groups with compounds of the general formula  $X:(CH)_{2n+1}Y$  in which X represents a substituted imino group, Y represents an arylamino group and n is a positive integer.

By condensing one molecular proportion of such a compound as is formulated above with one molecular proportion of a heterocyclic ammonium salt containing a reactive methyl group, or by condensing one molecular proportion of a salt of a compound represented by the above formula with one molecular proportion of a heterocyclic nitrogen compound containing a reactive external methylene group (a "methylene base") we obtain our new intermediate compounds in the form of salts. Further in accordance with our invention we cause these new intermediate compounds to interact with a molecular proportion of the same or a different methylene base. We thus obtain "symmetrical" or "unsymmetrical" polymethine dyestuffs according as the methylene bases are the same or different. Alternatively, we may

transform our new intermediate compounds into the corresponding bases and cause these to interact with any desired heterocyclic ammonium compounds containing a reactive methyl group.

Another way of carrying our invention into effect comprises the direct production of dyestuffs by the interaction of the compound represented by the formula  $X:(CH)_{2n+1}Y$  or a salt of it, with any of the components previously mentioned, it being understood that eventually at least one molecule of an acidic substance or residue must be present to ensure the formation of the dyestuff. Thus, one molecular proportion of the compound  $X:(CH)_{2n+1}Y$  may be condensed with two of a methylene base either in the presence of one molecular proportion of mineral acid, or in acetic anhydride which provides sufficient acid for the transformation; but if a salt of the compound  $X:CH_{2n+1}Y$  is used in the first place no other acid is necessary or indeed advisable. If it is desired to condense the compound or a salt thereof with two molecules of a heterocyclic ammonium salt containing a reactive methyl group it is advantageous to carry out the condensation in presence of an acid binding agent e.g. a base or the salt of a weak acid. We further find that as what may be called the second component there may be employed, in addition to compounds containing an external reactive methylene group, cyclic compounds with intracyclic reactive methylene groups, such as pyrazolones, or bodies capable of reacting tautomerically as though such groups were present, e.g. indoles not substituted in the  $\beta$ -position.

We obtain "unsymmetrical" dyestuffs in a single operation when we cause to interact a compound of the formula

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X : (CH)<sub>2n+1</sub>Y with a mixture in equivalent proportions of a heterocyclic ammonium salt containing a reactive external methyl group, and a methylene base or an indole not substituted in the  $\beta$ -position.

Our invention is illustrated but not limited by the following examples in which the parts are by weight.

#### EXAMPLE 1.

A solution of 285 parts of 5-anilino-1-phenylimino -  $\Delta^{2:4}$ -pentadiene hydrochloride and 350 parts of 1:3:3-trimethyl-2-methylene-indoline in 200 parts of acetic anhydride is heated at 100° C. for 45 mins. and then at the boil for 5 mins. The product is poured into water, 10 pts. by vol. of concentrated hydrochloric acid are added, followed by a concentrated aqueous solution of 32 pts. by weight of potassium iodide. The precipitated dye is filtered off. It dyes tanned cotton bright green, fast to acids.

#### EXAMPLE 2.

A solution of 25 parts of  $\beta$ -anilino-acrolein anil and 30 parts of 2:3:3-trimethylindolenine methiodide in 200 parts of acetic anhydride is heated to boiling for one hour. The solution becomes bright green in colour. It is diluted with ether and the intermediate compound so precipitated, presumably as its acetyl compound, is heated with water containing a little hydrochloric acid, cooled and filtered. The product is a dark green powder.

#### EXAMPLE 3.

The trimethylindolenine methiodide used in example 2 is replaced by an equal weight of 2-methyl-benzthiazole ethiodide; the solution assumes an olive green tint on boiling. Water is added and the intermediate which is precipitated is filtered off.

#### EXAMPLE 4.

The intermediate obtained in example 2 is dissolved in 10 parts of acetic anhydride and heated with a molecular proportion of 2-methyl-benzthiazole ethiodide and potassium acetate. The dye obtained dyes tannin-mordanted cotton a bright greenish blue. The same dye is obtained in a similar manner from the intermediate from example 3 and 1:3:3-trimethyl-2-methyleneindoline.

#### EXAMPLE 5.

To the solution obtained by heating together 25 parts of  $\beta$ -anilino-acrolein anil and 30 parts of 2:3:3-trimethylindolenine methiodide in 200 parts of acetic anhydride for 1 hour is added 13 parts of  $\alpha$ -methylindole. The mixture is boiled for one hour. The crystalline dye is filtered from the cooled liquor. It dyes tanned cotton a lavender blue shade.

Dated the 24th day of February, 1930.

E. C. G. CLARKE,

Imperial Chemical House, Millbank,  
London, S.W. 1,

Solicitor for the Applicants.

### PROVISIONAL SPECIFICATION.

No. 16,912, A.D. 1930.

### Improvements in or relating to the Manufacture of Photographic Sensitisers.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company incorporated under the laws of Great Britain and HENRY ALFRED PIGGOTT, and ERNEST HARRY RODD, both of Crumpsall Vale Chemical Works, Blackley, Manchester, both British Subjects, do hereby declare the nature of this invention to be as follows:—

According to the present invention we have found that the products of our co-pending application No. 6083/30 with which the present application is cognate, are valuable photographic sensitisers. We treat a photographic emulsion, such

as a sensitive in the untreated state to rays of light of wave lengths between 360 and 500 millimicrons, with, for example, the product of example 1 of our said co-pending application 6083/30, and obtain an emulsion sensitive not only to light of the original range of wave lengths, but showing also a remarkable sensitivity to a band of light of wave lengths lying between 750 and 800 millimicrons.

Dated this 31st day of May, 1930.

A. E. BINGER,

Imperial Chemical House, Millbank,  
London, S.W. 1,

Solicitor for the Applicants.

## COMPLETE SPECIFICATION

# Manufacture of Intermediates and Dyes from Heterocyclic Nitrogen Compounds.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain and HENRY ALFRED PIGGOTT, and ERNEST HARRY RODD, both of Crumpsall Vale Chemical Works, Blackley, Manchester, both British Subjects, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention comprises the manufacture of new intermediate compounds and dyes of the polymethine series therefrom.

We have discovered that valuable new intermediate compounds and dyes are obtained by condensing heterocyclic nitrogen compounds containing reactive methyl groups or external reactive methylene groups with compounds of the general formula  $X:(CH)_{2n+1}Y$  in which X represents a substituted imino group, Y represents an arylamino group and  $n$  is a positive integer. We have further found that those of the products described above as are dyestuffs are valuable photographic sensitizers.

By condensing one molecular proportion of such a compound as is formulated above with one molecular proportion of a heterocyclic ammonium salt containing a reactive methyl group, or by condensing one molecular proportion of a salt of a compound represented by the above formula with one molecular proportion of a heterocyclic nitrogen compound containing a reactive external methylene group (a "methylene base") we obtain our new intermediate compounds in the form of salts. Further in accordance with our invention we cause these new intermediate compounds to interact with a molecular proportion of the same or a different methylene base. We thus obtain "symmetrical" or "unsymmetrical" polymethine dyestuffs according as the methylene bases are the same or different. Alternatively, we may transform our new intermediate compounds into the corresponding bases and cause these to interact with any desired heterocyclic ammonium compounds containing a reactive methyl group.

Another way of carrying our invention into effect comprises the direct pro-

duction of dyestuffs by the interaction of the compound represented by the formula  $X:(CH)_{2n+1}Y$  or a salt of it, with any of the heterocyclic nitrogen components previously mentioned, it being understood that eventually at least one molecule of an acidic substance or residue must be present to ensure the formation of the dyestuff. Thus, one molecular proportion of the compound  $X:(CH)_{2n+1}Y$  may be condensed with two of a methylene base either in the presence of one molecular proportion of mineral acid, or in acetic anhydride which provides sufficient acid for the transformation; but if a salt of the compound  $X:(CH)_{2n+1}Y$  is used in the first place no other acid is necessary or indeed advisable. If it is desired to condense the compound or a salt with two molecules of a heterocyclic ammonium salt containing a reactive methyl group it is advantageous to carry out the condensation in presence of an acid binding agent, e.g. a base or the salt of a weak acid. We further find that as what may be called the second component there may be employed, in addition to compounds containing an external reactive methylene group, cyclic compounds with intracyclic reactive methylene groups, such as pyrazolones, or bodies capable of reacting tautomerically as though such groups were present, e.g. indoles not substituted in the  $\beta$ -position.

We obtain "unsymmetrical" dyestuffs in a single operation when we cause to interact one molecular proportion of a compound of the formula  $X:(CH)_{2n+1}Y$  with a mixture consisting of one molecular proportion of a heterocyclic ammonium salt containing a reactive external methyl group, and one molecular proportion of a methylene base of a different heterocyclic ammonium salt or an indole not substituted in the  $\beta$ -position.

Our invention is illustrated but not limited by the following examples in which the parts are by weight.

## EXAMPLE 1.

A solution of 285 parts of 5-anilino-1-phenylimino- $\Delta^{2:4}$ -pentadiene hydrochloride and 350 parts of 1:3:3-trimethyl-2-methylene-indoline in 200 parts of acetic anhydride is heated at 100° C. for 45 mins. and then at the boil for 5 mins. The product is poured into water,

10 pts. by vol. of concentrated hydrochloric acid are added, followed by a concentrated aqueous solution of 32 pts. by weight of potassium iodide. The precipitated dye is filtered off. It dyes tanned cotton bright green, fast to acids.

A photographic plate such as is sensitive in the untreated state to rays of light of wave length between 360 and 500 millimicrons is treated with a dilute aqueous alcoholic solution of the above product in the usual way in which sensitising dyestuffs are applied and dried. The so-treated photographic plate then exhibits, in addition to its original sensitivity, remarkable sensitivity to a band of light of wave lengths lying between 750 and 900 millimicrons.

#### EXAMPLE 2.

A solution of 25 parts of  $\beta$ -anilino-acrolein anil and 30 parts of 2:3:3-trimethylindolenine methiodide in 200 parts of acetic anhydride is heated to boiling for one hour. The solution becomes bright green in colour. It is diluted with ether and the intermediate compound so precipitated, presumably as its acetyl compound, is heated with water containing a little hydrochloric acid, cooled and filtered. The product is a dark green powder.

#### EXAMPLE 3.

The trimethylindolenine methiodide used in example 2 is replaced by an equal weight of 2-methyl-benzthiazole ethiodide; the solution assumes an olive green tint on boiling. Water is added and the intermediate which is precipitated is filtered off.

#### EXAMPLE 4.

The intermediate obtained in example 2 is dissolved in 10 parts of acetic anhydride and heated with a molecular proportion of 2-methyl-benzthiazole ethiodide and potassium acetate. The dye obtained dyes tannin-mordanted cotton a bright greenish blue. The same dye is obtained in a similar manner from the intermediate from example 3 and 1:3:3-trimethyl-2-methyleneindoline.

#### EXAMPLE 5.

To the solution obtained by heating together 25 parts of  $\beta$ -anilino-acrolein anil and 30 parts of 2:3:3-trimethylindolenine methiodide in 200 parts of acetic anhydride for 1 hour is added 13 parts of  $\alpha$ -methylindole. The mixture is boiled for one hour. The crystalline dye is filtered from the cooled liquor. It dyes tanned cotton a lavender blue shade.

#### EXAMPLE 6.

A solution of 17.5 parts of 1:3:3-tri-

methyl-2-methyleneindoline and 13 parts of  $\beta$ -anilino-acrolein-anil hydrochloride in 100 parts of acetic anhydride is heated to 100° for 1½ hours. The acetic anhydride is removed by distillation at a diminished pressure. The residuum is washed with warm water. It is then dissolved in concentrated hydrochloric acid and reprecipitated by dilution with water. Yield 15 parts.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of new intermediate compounds by condensing heterocyclic nitrogen compounds containing reactive methyl groups or external reactive methylene groups with a molecular proportion of a compound of

the general formula  $\begin{matrix} X \\ Y \end{matrix} > (CH)_n + 1$  wherein

X represents a substituted imino group, Y represents an arylamino group, and n is a positive integer.

2. Process for the manufacture of new dyestuffs by condensing heterocyclic nitrogen compounds containing reactive methyl groups or external reactive methylene groups with one-half molecular proportion of a compound  $\begin{matrix} X \\ Y \end{matrix} > (CH)_n + 1$  as defined in Claim 1.

3. Process for the manufacture of new dyestuffs by condensing the products of Claim 1 with a molecular proportion of a heterocyclic nitrogen compound containing reactive methyl or external reactive methylene groups, or a cyclic compound which contains an inter-cyclic reactive methylene group (e.g. a pyrazolone) or which reacts tautomerically as though such a group were present (e.g. an indole not substituted in the  $\beta$ -position).

4. New intermediates and dyestuffs whenever obtained by the process of any of the preceding claims or by the obvious chemical equivalent of such process.

5. Process for the manufacture of photographic emulsions sensitive to light of long wave length which comprises the application to a photographic emulsion of dyestuffs claimed in Claim 4.

6. Photographic emulsions, sensitive to light of long wave lengths containing a dyestuff or dyestuffs claimed in Claim 4.

7. Materials dyed with the dyestuffs of Claim 4.

Dated this 24th day of December, 1930.

E. C. G. CLARKE,  
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Solicitor for the Applicants.